Complexes of Functional Phosphines. 4. Coordination Properties of (Diphenylphosphino)acetonitrile, Ethyl (Diphenylphosphino)acetate, and Corresponding Carbanions. Characterization of a New Facile Reversible CO_2 Insertion into Palladium(II) Complexes

Pierre Braunstein,*[2a] Dominique Matt,[2a] Yves Dusausoy,[2b] Jean Fischer,[2c] André Mitschler,[2c] and Louis Ricard[2c]

Contribution from the Laboratoire de Chimie de Coordination, Associé au CNRS (ERA 670), Université Louis Pasteur, 67070 Strasbourg Cédex, France, the Laboratoire de Minéralogie-Cristallographie, Associé au CNRS (ERA 162), Université de Nancy 1, C.O. 140, 54037 Nancy, France, and the Laboratoire de Cristallochimie, Associé au CNRS (ERA 08), Université Louis Pasteur, 67070 Strasbourg Cédex, France. *Received December 12, 1980. Revised Manuscript Received March 23, 1981*

Abstract: The coordination properties of Ph_2PCH_2CN (L^1) and $Ph_2PCH_2COOC_2H_5$ (L^2) have been investigated. Complexes have been prepared and characterized in which they behave either as monodentate ligands through the phosphorus only, as in $(aph)PdClL^2$ (aph-H = acetophenone *N*-phenylhydrazone), Pd(dmba)ClL (dmba-H = dimethylbenzylamine), and Pd(8-mq)BrL^2 (8-mq-H = 8-methylquinoline), or as bidentate ligands through the phosphorus and the functional group Y (Y = CN, $COOC_2H_5$), as in $[Pd(dmba)L^1]_2(PF_6)_2$, $[Pd(dmba)L^2]PF_6$, and $[Pd(8\text{-mq})L^2]PF_6$. The carbanions $(Ph_2PCHY)^-$ derived from L^1 and L^2 were prepared and reacted with the dinuclear $[Pd(\overline{\mathrm{C\ N}})X]_2$ complexes ($\overline{\mathrm{C\ N}}$ = dmba, X = Cl; $\overline{\mathrm{C\ N}}$ = 8-mq, X = Br). When the ratio Pd/L^- = 2 was used, dinuclear complexes of the general formula $(\overline{\mathrm{C\ N}})\mathrm{Pd}(\mu\text{-X})(\mu\text{-}\overline{\mathrm{PPh_2CHY}})\mathrm{Pd}(\overline{\mathrm{C\ N}})$ were formed. For $\overline{\mathrm{C\ N}}$ = dmba, X = Cl, and Y = $COOC_2H_5$, the molecular structure of complex **10** has been determined by X-ray diffraction: monoclinic, space group C_{2h}^5—$P2_1/C$ with $Z = 4$, $a = 10.036$ (4) Å, $b = 34.000$ (9) Å, $c = 10.297$ (4) Å, $\beta = 106.82$ (2)°, ρ(calcd) = 1.556 g/cm^3. The structure was solved by using 2015 reflections with $I > 3\sigma(I)$ and refined to conventional $R = 0.075$. The functional carbanion bridges the two palladium units with Pd(1)–P = 2.233 (6) Å and Pd(2)–C(13) = 2.01 (2) Å, whereas the bridging Cl is trans with respect to the two Pd–C σ bonds of the cyclometalated ligands. When the ratio $Pd/[L^2]^-$ = 1 was used, mononuclear complexes of the general formula $(\overline{\mathrm{C\ N}})\overline{\mathrm{Pd[Ph_2PCHC(O}}\mathrm{)OC_2H_5]}$ were obtained. For $\overline{\mathrm{C\ N}}$ = dmba, the molecular structure of complex **13** has been determined by X-ray diffraction: orthorhombic, D_{2h}^1—*Pbca* with $Z = 8$, $a = 17.285$ (5) Å, $b = 17.026$ (5) Å, $c = 15.687$ (4) Å, ρ(calcd) = 1.476 g/cm^3. The structure was solved by using 2037 reflections with $I > 3\sigma(I)$ and refined to conventional $R = 0.056$. The functional carbanion acts now as a (*P*, *O*) chelate ligand, with Pd–P = 2.242 (2) Å and Pd–O = 2.117 (5) Å, the phosphorus being trans with respect to the Pd–N bond. Complex **13** was reacted with $[Pd(\overline{\mathrm{C\ N}})X]_2$, affording the dinuclear complexes $\mathrm{(dmba)Pd(\mu\text{-}X)(\mu\text{-}\overline{Ph_2PCH\text{-}(COOC_2H_5)}Pd(\overline{C\ N})}$, showing the nucleophilic character of the carbon atom in a position α to the phosphorus. This was further shown by the reaction of **13** with CO_2 in THF under ambient conditions leading to the CO_2-insertion product **16** ($\mathrm{(dmba)\overline{Pd[Ph_2PC(CO_2C_2H_5)C(O}})OH]$). The analogous complex **17** ($\mathrm{(8\text{-}mq)\overline{Pd[Ph_2PC(CO_2C_2H_5)C(O}})OH]$), was obtained in a similar way from complex **14** ($\mathrm{(8\text{-}mq)\overline{Pd[Ph_2PCHC(O}})OC_2H_5]$). The molecular structure of **17** was established by X-ray diffraction: triclinic, C_i^1—$P\bar{1}$ with $Z = 4$, $a = 12.206$ (2) Å, $b = 15.113$ (2) Å, $c = 15.156$ (5) Å, $\alpha = 108.47$ (1)°, $\beta = 105.36$ (3)°, $\gamma = 99.05$ (2)°, ρ(calcd) = 1.46 g/cm^3. The structure was solved by using 2442 reflections with $I > 2\sigma(I)$ and refined to conventional $R = 0.070$. CO_2 insertion occurs with C–C coupling to the nucleophilic α-phosphino carbon of the ligand and formation of a new five-membered ring Pd,P,C(12),C(11),O(1), the ester function no longer interacting with the palladium atom. Spectroscopic IR and ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR data are discussed in relation with the structure and the reactivity of the new complexes. Both **16** and **17** in THF solution liberate CO_2 when argon is bubbled through under ambient conditions, regenerating **13** and **14**, respectively. The new CO_2 carriers **13** and **14** therefore provide the first examples where reversible CO_2 fixation by a transition-metal complex has been fully characterized by X-ray diffraction and shown to occur via carbon–carbon bond formation.

The transition-metal coordination chemistry of tertiary phosphines with functional substituents, e.g. esters,[3,4] nitriles,[5] ethers,[6] alkene,[7-9] alkynes,[10] ketones,[11] and aldehydes,[12] has aroused considerable interest in the recent past. This is due largely to the expected electronic and/or steric effects of the function. Their evaluation in transition-metal complexes may allow us to determine the role of the function on the overall properties of the metal-ligand system. In dealing with R_2PCH_2Y ligands (in which Y

---

[1] Part 3: Braunstein, P.; Matt, D.; Fischer, J.; Ricard, L.; Mitschler, A. *Nouv. J. Chim.* **1980**, *4*, 493.

[2] (a) Laboratoire de Chimie de Coordination, ERA 670 CNRS, Université Louis Pasteur. (b) Laboratoire de Minéralogie-Cristallographie, Université de Nancy. (c) Laboratoire de Cristallochimie, Université Louis Pasteur.

[3] Empsall, H. D.; Hyde, E. L.; Pawson, D.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1292–1298.

[4] Braunstein, P.; Matt, D.; Mathey, F.; Thavard, D. *J. Chem. Res., Synop.* **1978**, 232–233; *J. Chem. Res., Miniprint* **1978**, 3041–3063.

[5] Cheng, K.; Foxman, B. M. *J. Am. Chem. Soc.* **1977**, *100*, 8102–8103.

[6] Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1978**, *18*, 2658–2666.

[7] Charrier, C.; Mathey, F. *J. Organomet. Chem.* **1977**, *128*, C41–C43.

[8] Mathey, F.; Santini, C. *Can. J. Chem.* **1979**, *57*, 753–759.

[9] Bennet, M. A.; Johnson, R. N.; Tomkins, I. B. *Inorg. Chem.* **1975**, *14* 1908–1915.

[10] Carty, A. J.; Paik, H. N.; Palenik, G. J. *Inorg. Chem.* **1977**, *16*, 300–305.

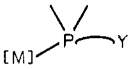
[11] Empsall, H. D.; Johnson, S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 302–307.

[12] Rauchfuss, T. B. *J. Am. Chem. Soc.* **1979**, *101*, 1045–1047.

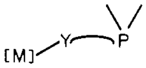
0002-7863/81/1503-5115$01.25/0

has potential donor properties), we have to examine the following features: donor/acceptor effects of Y on the coordination properties of the phosphino group; facilited C–H activation of the adjacent methylene group; evaluation of the bonding modes of the Y function.

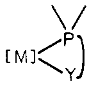
In the general case the behavior of such a ligand will be as depicted in compounds Ia, b, II, and III.



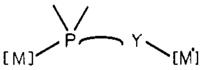
Ia



Ib



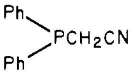
II



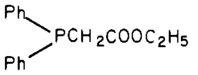
III

With late transition-metal elements, the monodentate situation Ia is more frequent than Ib. Nevertheless an example of the latter has been described[13] recently for M = Rh and Y = SO_3^- and is relevant to the preparation of water-soluble catalysts. When coordination properties of P and Y toward a given metal are different, a type II structure can lead to a type I structure through a facile M–Y (or M–P) cleavage and therefore create a vacant site at the metal. These ligands have been called hemilabile[6] and may play an important role in homogeneous catalysis. Clearly in a type III structure the bridging ligand introduces a dissymmetry in the molecule. An appropriate choice of the other ligands might enhance this effect. This can also be achieved when M and M′ are metals of different types, thus making accessible new mixed heterobimetallic systems with or without metal–metal bonds.

We have reported[4] the study of complexes of diphenylphosphinoacetonitrile L^1 or ethyl diphenylphosphinoacetate L^2



L^1



L^2

with transition metals such as Fe(0), Au(I) Ni(II), Pd(II), Pt(II), Ir(III), and Rh(III). All these complexes were of structure Ia except those of Ir(III) and Rh(III) with L^2, which were of type II, the latter showing an interesting stereodynamic behavior and illustrating the hemilabile character of L^2. We present here further examples of Pd(II) complexes with these ligands. Our studies have been extended to the α-carbanions derived from L^1 and L^2, prepared from either the free or coordinated ligands. In a preliminary communication[14] we have described the reaction of $(L^1)^-$ and $(L^2)^-$ with *cis*-$PtCl_2(PhCN)_2$ leading unexpectedly to reaction with the coordinated nitrile. In this work we also report new reactions of these carbanions with cyclometalated Pd(II) compounds, affording new structures of types II and III. Their reactivity toward CO_2 fixation has been tested and indicates in two examples a reversible fixation under ambient conditions in THF. The CO_2 insertion product has been characterized crystallographically in one case.

Experimental Section

A. Reagents and Physical Measurements. All reactions were performed in Schlenk-type flasks under argon. Solvents were distilled under argon from sodium benzophenone ketyl prior to use except dichloromethane, chlorobenzene, and acetone, which were dried and distilled over P_2O_5. Ethanol was distilled from $Mg(OEt)_2$. Argon (Air Liquide purified grade) was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water. CO_2 was purchased from Air Liquide (N48).

Elemental analysis of C, H, N, and F were performed by the Service Central de Microanalyses du C.N.R.S..

Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer as KBr pellets (unless otherwise specified) and on a Polytec FIR 30 FT-interferometer as polythene disks in the region 420–50 cm^{-1}.

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}NMR spectra were recorded at 90.00 and/or 250.00, 62.86, and 36.43 MHz, respectively, on a FT-Brucker WH-90 or Cameca 250 instrument. Proton and carbon chemical shifts are positive downfield relative to external Me_4Si. Positive phosphorus chemical shifts indicate a downfield position relative to H_3PO_4.

B. Syntheses. Ligands. Ph_2PCH_2CN (L^1) and $Ph_2PCH_2C(O)OC_2H_5$ (L^2) were prepared by the method described previously.[4] Their NMR data are as follows.

L^1: ^{1}H NMR ($CDCl_3$) δ 2.78 (2 H, d, PCH_2, ^2J(PH) = 4.5 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −17.8; ^{13}C{^{1}H} NMR δ 16.19 (d, PC, ^1J(PC) = 28.5 Hz), 117.0 (CN, ^2J(PC) ≃ 5 Hz).

L^2: ^{1}H NMR ($CDCl_3$) δ 1.11 (3 H, t, ^3J = 7.0 Hz), 3.11 (2 H, s, PCH_2, ^2J(PH) = 0 Hz), 4.03 (2 H, q, ^3J = 7.0 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −16.6; ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 14.03 (s, CH_3CH_2), 35.23 (d, PCH_2, ^1J(PC) = 23.7 Hz), 60.93 (s, CH_2CH_3), 170.69 (d, C=O).

$Ph_2P(S)CH_2C(S)OC_2H_5$ (L^3) was prepared by refluxing a solution of $Ph_2P(O)CH_2C(O)OC_2H_5$ (3 g) in toluene (100 mL) with P_4S_{10} (6 g) for 8 h.[15] After being cooled, the mixture was filtered and neutralized with Na_2CO_3. The solvent was removed and the residue was chromatographed on Kieselgel, eluting with toluene. The product was obtained from the first fraction (2.2 g): ^{1}H NMR ($CDCl_3$) δ 1.10 (3 H, t, ^3J = 7.2 Hz), 4.17 (2 H, d, ^2J(PH) = 14.0 Hz), 4.27 (2 H, q, ^3J = 7.2 Hz, ^5J(PH) = 0.7 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$) δ +39.2; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 12.43 (s, CH_3), 51.33 (d, PCH_2, ^1J(PC) = 41.2 Hz), 68.06 (s, OCH_2), 209.02 (C=S).

Anal. Calcd for $C_{16}H_{17}OPS_2$: C, 59.98; H, 5.35. Found: C, 59.90; H, 5.45.

Complexes. $[Pd(\overset{\frown}{C\,N})X]_2$ (X = Cl, Br) complexes were prepared by previously described methods, for the following cyclometalated ($\overset{\frown}{C\,N}$) ligands: acetophenone *N*-phenylhydrazone (aph),[16] dimethylbenzylamine (dmba),[17] 8-methylquinoline (8-mq).[18]

Pd(aph)ClL^2 (1). To a suspension of $[Pd(aph)Cl]_2$ (0.370 g, 0.53 mmol) in CH_2Cl_2 (25 mL) was added dropwise L^2 (0.288 g, 1.06 mmol) in CH_2Cl_2 (5 mL). After 2 h of stirring, the clear solution was filtered. After concentration, pentane was added, affording a yellow-green, air-stable, powder of 1 (0.560 g, 89%) (mp 136–138 °C): IR ν(NH) 3210 (mbr), ν(CO) 1722 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 0.94 (3 H, t, CH_2CH_3, ^3J = 7.0 Hz), 2.33 (3 H, s, CCH_3), 3.76 (2 H, d, PCH_2, ^2J(PH) = 8.2 Hz), 3.77 (2 H, q, CH_2CH_3, ^3J = 7.0 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 29.0; ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 13.73 (s, CH_2CH_3), 15.29 (s, CH_3CN), 37.77 (d, PCH_2, ^1J(PC) = 29.6 Hz), 61.19 (s, CH_2CH_3).

Anal. Calcd for $C_{30}H_{30}ClN_2O_2PPd$: C, 57.75; H, 4.85; N, 4.58; Found: C, 54.44;[19] H, 5.15; N, 4.77.

Pd(dmba)ClL^1 (2). To a stirred suspension of $[Pd(dmba)Cl]_2$ (0.552 g, 1.0 mmol) in THF (30 mL) was added slowly L^1 (0.450 g, 2.0 mmol) in THF (10 mL). After 0.2 h, the mixture was filtered and pentane added to produce green-yellow, air-stable, crystals of **2**, which were dried in vacuo (0.920 g, 92%) (mp 99–100 °C): IR ν(CN) 2246 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.83 (6 H, d, ^4J(PH) = 2.9 Hz), 3.82 (2 H, d, PCH_2, ^2J(PH) = 9.4 Hz), 4.06 (2 H, d, NCH_2, ^4J(PH) = 2.6 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 33.8; ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 21.30 (d, PCH_2, ^1J(PC) = 25.9 Hz), 50.60 (s, $N(CH_3)_2$), 73.23 (s, NCH_2), 115.80 (d, C≡N, ^2J(PC) ≃ 7 Hz).

Anal. Calcd for $C_{23}H_{24}ClN_2PPd$: C, 55.11; H, 4.83; N, 5.59. Found: C, 55.00; H, 4.90; N, 5.70.

Pd(dmba)ClL^2 (3). To a stirred suspension of $[Pd(dmba)Cl]_2$ (0.552 g, 1.0 mmol) in CH_2Cl_2 (20 mL) was added dropwise a solution of L^2 (0.544 g, 2 mmol). This mixture was stirred for 0.2 h and filtered and the solvent removed in vacuo. The residue was washed with pentane and recrystallized from toluene/pentane, affording a pale yellow, air-stable, powder of **3** (0.888 g, 81%) (mp 90–92 °C): IR ν(CO) 1733 (s), 1721 (vs) cm^{-1}; far-IR bands 373 (m), 362 (m), 294 (s), 265 (w), 241 (m), cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.03 (3 H, t, ^3J = 7.0 Hz), 2.79 (6 H, d, ^4J(PH) = 2.9 Hz), 3.82 (2 H, d, ^2J(PH) = 10.6 Hz), 3.83 (2 H, q, ^3J = 7.0 Hz), 4.04 (2 H, d, ^4J(PH) = 2.3 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 31.8; ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 13.94 (s, CH_2CH_3), 37.94 (d, PCH_2, ^1J(PC) = 27.7 Hz), 50.51 (s, $N(CH_3)_2$), 61.22 (s, CH_2CH_3), 73.38 (s, NCH_2), 168.27 (s, C=O).

Anal. Calcd for $C_{25}H_{29}ClNO_2PPd$: C, 54.76; H, 5.33; N, 2.55.

---

(13) Borowski, A. F.; Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chim.* **1977**, *2*, 137–144.

(14) Braunstein, P.; Matt, D.; Dusausoy, Y.; Protas, J. *J. Chem. Soc., Chem. Commun.* **1979**, 763–764.

(15) Mathey, F., private communication.

(16) Braunstein, P.; Dehand, J.; Pfeffer, M. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 521–524.

(17) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909–913.

(18) Hartwell, G. E.; Lawrence, R. V.; Smas, M. J. *J. Chem. Soc. D* **1970**, 912.

(19) Experimental C analysis results which are lower than required by theory have also been found in related complexes.[20]

(20) Dehand, J.; Pfeffer, M.; Zinsius, M. *Inorg. Chim. Acta* **1975**, *13*, 229–332.

(21) SHELX Crystallographic Calculation Program, G. M. Sheldrick, University of Göttingen, West Germany.

(22) See paragraph at the end of paper regarding supplementary material.

Found: C, 54.70; H, 5.21; N, 2.54.

Pd(8-mq)BrL^2 (4). To a stirred suspension of $[Pd(8\text{-mq})Br]_2$ (0.657 g, 1.0 mmol) in THF (30 mL) was added a solution of L^2 (0.545 g, 2.0 mmol) in THF (10 mL). After 0.2 h, this solution was filtered and pentane added, affording yellow crystals of **4** (air-stable). These were recrystallized from CH_2Cl_2/pentane (1.05 g, 87%) (mp 141–143 °C): IR ν(CO) 1711 (s), ν(PdBr) 172 (s) or 161 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.05 (3 H, t, ^3J = 7.3 Hz), 3.02 (2 H, d, CH_2Pd, ^3J(PH) = 3.8 Hz), 3.93 (2 H, d, PCH_2, ^2J(PH) = 10.0 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 28.7; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 13.84 (s, $CH_2\mathit{C}H_3$), 34.25 (s, CH_2Pd), 37.34 (d, PCH_2, ^1J(PC) = 27.5 Hz), 61.22 (s, $\mathit{C}H_2CH_3$), 168.28 (d, C=O, ^2J(PC) = 4.6 Hz).

Anal. Calcd for $C_{26}H_{25}BrNO_2PPd$: C, 51.98; H, 4.19; N, 2.33. Found: C, 51.75; H, 4.15; N, 2.42.

[Pd(dmba)(L^2)]PF$_6$ (5). To a solution of **3** (0.274 g, 0.5 mmol) in CH_2Cl_2 (30 mL) was added a suspension of $AgPF_6$ (0.139 g, 0.55 mmol) in CH_2Cl_2 (10 mL). After ca. 0.5 h, the solution was filtered to remove AgCl and then was concentrated. Addition of pentane gave a pale yellow powder which was recrystallized from CH_2Cl_2/pentane to afford air-stable **5** (0.259 g, 79%) (mp 80 °C dec): IR (Nujol mull) ν(CO) 1651 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.35 (3 H, t, ^3J = 7.3 Hz), 2.93 (6 H, d, ^4J(PH) = 2.9 Hz), 3.86 (2 H, d, ^2J(PH) = 11.1 Hz), 4.08 (2 H, d, ^4J(PH) = 2.3 Hz), 4.41 (2 H, q, ^3J = 7.2 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 26.4 (s, PdP), −142.6 (sept, ^1J(PF) = 710.5 Hz); $^{13}C\{^1H\}$ NMR δ 13.64 (s, $CH_2\mathit{C}H_3$), 40.69 (d, ^1J(PC) = 33.3 Hz), 50.48 (s, $N(CH_3)_2$), 66.93 (s, $\mathit{C}H_2CH_3$), 70.49 (s, NCH_2).

Anal. Calcd for $C_{25}H_{29}F_6NO_2P_2Pd$: C, 45.64; H, 4.44; N, 2.13. Found: C, 45.73; H, 4.49; N, 2.19.

[Pd(8-mq)L^2]PF$_6$ (6). To a stirred solution of **4** (0.300 g, 0.5 mmol) in CH_2Cl_2 (20 mL) was added a suspension of $AgPF_6$ (0.139 g, 0.55 mmol) in CH_2Cl_2 (10 mL). After 0.5 h of stirring the mixture was filtered. The addition of pentane gave, after cooling at −10 °C, white crystals of **6** (0.05 g, 15%) (mp 98–100 °C): IR ν(CO) 1628 (sbr) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.41 (3 H, t, ^3J = 7.3 Hz), 3.59 (2 H, d, CH_2Pd, ^3J(PH) = 3.9 Hz), 3.92 (2 H, d, PCH_2, ^2J(PH) = 11.2 Hz), 4.44 (2 H, q, ^3J = 7.3 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 24.5 (s, PdP), −142.5 (sept, PF_6, ^1J(PF) = 711 Hz); ^{13}C NMR (CD_2Cl_2) δ 13.64 (q, $CH_2\mathit{C}H_3$, ^1J(CH) ≃ 123 Hz), 25.24 (t, CH_2Pd, ^1J(CH) ≃ 139 Hz), 39.37 (t of d, PCH_2, ^1J(PC) = 31.4 Hz, ^1J(CH) ≃ 134 Hz), 66.87 (t, $\mathit{C}H_2CH_3$, ^1J(CH) ≃ 154 Hz), 180.50 (d, C=O, ^2J(PC) ≃ 10 Hz).

Anal. Calcd for $C_{26}H_{25}F_6NO_2P_2Pd$: C, 46.90; H, 3.79; N, 2.10. Found: C, 46.96; H, 3.70; N, 2.16.

[Pd(dmba)L^1]$_2$(PF$_6$)$_2$ (7). To a stirred solution of **2** (0.251 g, 0.50 mmol) in CH_2Cl_2 (30 mL), was added a suspension of $AgPF_6$ (0.139 g, 0.55 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 0.5 h and carefully filtered. The solvent was then removed in vacuo, and the white product **7** was washed with pentane and dried (0.025 g, 8%) (mp 215 °C dec): IR ν(CN) 2298 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.93 ($N(CH_3)_2$, ^4J(PH) = 2.9 Hz). More data were precluded by the very low solubility of **7**.

Anal. Calcd for $C_{46}H_{48}F_{12}N_4P_4Pd_2$: C, 45.23; H, 3.96; N, 4.59. Found: C, 45.25; H, 4.08; N, 4.69.

Preparation of a Standard Solution of (L^1)$^-$ (A). To a solution of dry *N*-isopropylcyclohexylamine (0.706 g, 5.0 mmol) in THF (25 mL) was added dropwise at −20 °C a 1.73 M hexane solution of *n*-C_4H_9Li (2.9 mL). After ca. 0.5 h, this solution was added dropwise at −5 °C to a solution of L^1 (1.125 g, 5 mmol) in THF (25 mL). In the following, solution A will be considered as containing mainly the carbanion (L^1)$^-$ with some unreacted L^1.

Preparation of a Standard Solution of (L^2)$^-$ (B). The procedure used was similar to that described for (L^1)$^-$, using 1.361 g (5.0 mmol) L^2.

Pd(dmba)(μ-Cl)[μ-Ph$_2$PCH(CN)]Pd(dmba) (8). To a stirred suspension of $[Pd(dmba)Cl]_2$ (1.104 g, 2.0 mmol) in THF (30 mL) was added at −10 °C 20 mL of solution A. This solution was stirred for 0.5 h, and pentane (100 mL) was added. After 3 h at room temperature, white, air-stable, crystals of **8** were collected and recrystallized from THF/pentane (0.960 g, 65% based on Pd) (mp 244 °C dec): IR ν(CN) 2192 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.50 (3 H, s, $CH_3{}^aNPdC^*$), 2.60 (3 H, s, $CH_3{}^bNPdC^*$), 2.73 (3 H, d, $CH_3{}^aNPdP$, ^4J(PH) = 2.1 Hz), 2.96 (3 H, d, $CH_3{}^bNPdP$, ^4J(PH) = 2.9 Hz), 3.63 (2 H, s, CH_2NPdC^*), 3.64 ((1 H, d, PCH, ^2J(PH) = 13.8 Hz), δ_A 3.67 and δ_B 4.45 (2 H, ABX spin system, $C\mathit{H^AH^B}NPdP$, $J(H^AH^B)$ = 13.5 Hz, $^4J(PH^A)$ ≃ 0 Hz, $^4J(PH^B)$ ≃ 1 Hz); $^{31}P\{^1H)$ NMR (CD_2Cl_2) δ 52.0 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 14.51 (d, ^1J(PC) = 20.34 Hz), 49.60 (s, NCH_3), 50.16 (s, NCH_3), 51.04 (s, NCH_3), 51.43 (s, NCH_3), 71.76 (s, NCH_2), 72.40 (s, NCH_2).

Anal. Calcd for $C_{32}H_{35}ClN_3PPd_2$: C, 51.88; H, 4.76; N, 5.67. Found: C, 51.99; H, 4.71; N, 5.79.

Complex 9 (See Results and Discussion). This compound was obtained in variable amounts (yield 20–30%) when at −10 °C 40 mL of solution A was added to a stirred suspension of $[Pd(dmba)Cl]_2$ (1.104 g, 2.0 mmol) in THF (50 mL). This solution was stirred for 0.5 h and pentane added, affording crystals of complex **8**. After isolation of **8** and further addition of pentane, yellow-green crystals of **9** precipitated. These were recrystallized from CH_2Cl_2/pentane, affording stable pale yellow crystals in **9** (mp 168 °C dec): IR ν(NH) 3285 (s), ν(CN) 2158 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.86 (6 H, d, $N(CH_3)_2$, ^2J(PH) = 2.6 Hz), 3.02 (6 H, d, $N(CH_3)_2$, ^2J(PH) = 2.2 Hz), 4.01 (6 H, unresolved signals); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 40.3 and 44.2; $^{13}C\{^1H\}$ NMR δ 36.0 (center of 4 signals; tentative assignment, two different P–C groups), 51.13 and 51.69 (2 signals; tentative assignment, two different $N(CH_3)_2$ groups), 73.17 and 73.75 (2 signals; tentative assignment, two different NCH_2 groups).

Pd(dmba)(μ-Cl)(μ-Ph$_2$PCH(CO$_2$C$_2$H$_5$)Pd(dmba) (10). To a stirred suspension of $[Pd(dmba)Cl]_2$ (0.552 g, 1.0 mmol) in THF (20 mL) was added at −20 °C 10 mL of solution A. Solubilization rapidly occurred, and after 5 h of stirring, pentane was added to produce white crystals of **10** which were collected and recrystallized from THF/pentane (0.481 g, 61% based on Pd). Suitable single crystals for X-ray diffraction were obtained from THF/pentane at 20 °C (mp 205–209 °C dec): IR ν(CO) 1672 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.19 (3 H, t, ^3J = 7.0 Hz), 2.46 (3 H, s, $CH_3{}^aNPdC^*$), 2.53 (3 H, s, $CH_3{}^bNPdC^*$), 2.72 (3 H, d, $CH_3{}^aNPdP$, $^4J(PH^a)$ = 1.5 Hz), 2.97 (3 H, d, $CH_3{}^bNPdP$, $^4J(PH^b)$ = 3.0 Hz), 3.03 (1 H, d, PCH, ^2J(PH) = 11.4 Hz), δ_A 3.52 and δ_B 3.65 (2 H, AB spin system, $CH^AH^BNPdC^*$, J(AB) = 13.6 Hz), δ_A 3.97 and δ_B 3.62 (2 H, ABX spin system, CH^AH^BNPdP, J(AB) = 13.6 Hz, $^4J(PH^A)$ ≃ 0 Hz, $^4J(PH^B)$ = 3.4 Hz), 4.05 (2 H, $OC\mathit{H}_2CH_3$, center of the AB part of an ABX_3 spin system); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 50.7; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 14.74 (s, $\mathit{C}H_3CH_2O$), 36.61 (d, PC, ^1J(PC) = 24.4 Hz), 49.52 (d, H_3C^ANPdP, $^3J(PC^A)$ ≃ 4 Hz), 49.86 (s, $H_3\mathit{C}^ANPdC^*$), 51.17 (s, $H_3\mathit{C}^BNPdC^*$), 51.53 (d, H_3C^BNPdP, $^3J(PC^B)$ ≃ 3 Hz), 59.33 (s, OCH_2), 72.00 (s, $\mathit{C}H_2NPdC^*$), 72.58 (d, CH_2NPdP, ^3J(PC) ≃ 3 Hz), 175.21 (d, C=O), ^2J(PC) = 6.1 Hz).

Anal. Calcd for $C_{34}H_{40}ClN_2O_2PPd_2$: C, 51.83; H, 5.12; N, 3.56. Found: C, 52.05; H, 4.90; N, 3.75.

Pd(8-mq)(μ-Br)[μ-Ph$_2$PCH(CN)]Pd(8-mq) (11). To a stirred suspension of $[Pd(8\text{-mq})Br]_2$ (0.657 g, 1.0 mmol) in THF (20 mL) was added 10 mL of solution A at −10 °C. Solubilization occurred, and after 0.3 h pentane (40 mL) was added, producing air-stable yellow-green crystals of **11** which were recrystallized from C_6H_5Cl/hexane (0.440 g, 55%) (mp 229–230 °C dec): IR ν(CN) 2173 (m) cm^{-1}; far-IR 329 (s), 265 (m), 244 (m), 203 (s), 172 (vs), 161 (sh) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ_A 3.00 and δ_B 3.11 (2 H, ABX spin system, CH^AH^BPdP, $^2J(H^AH^B)$ = 14.4 Hz, $^3J(PH^A)$ = 3.8 Hz, $^3J(PH^B)$ = 3.4 Hz), δ_A 2.95 and δ_B 3.23 (2 H, AB spin system, $CH^AH^BPdC^*$, $J(H^AH^B)$ = 14.8 Hz), 3.26 (1 H, PCH, ^2J(PH) = 8.0 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 35.3; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 1.44 (d, PC, ^1J(PC) = 10.7 Hz), 31.85 (s, CH_2Pd), 34.42 (s, CH_2Pd).

Anal. Calcd for $C_{34}H_{27}BrN_3PPd_2$: C, 50.97; H, 3.40; N, 5.24. Found: C, 51.23; H, 3.53; N, 5.05.

Pd(8-mq)(μ-Br)[μ-Ph$_2$PCH(CO$_2$C$_2$H$_5$)]Pd(8-mq) (12). To a stirred suspension of $[Pd(8\text{-mq})Br]_2$ (0.657 g, 1.0 mmol) in THF (20 mL) was added 10 mL of solution B at −10 °C. The reaction rapidly occurred, and after 0.3 h of stirring, pentane was added (150 mL), yielding a yellow air-stable powder. **12** was recrystallized from THF/pentane (0.407 g, 48%) (mp 209–211 °C dec): IR ν(CO) 1672 (s) cm^{-1}; far-IR bands 265 (s), 243 (m), 205 (m), 176 (vs) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.18 (3 H, t, ^3J = 7.2 Hz), δ_A 2.96 and δ_B 3.03 (2 H, ABX spin system, CH^AH^BPdP, $^3J(PH^A)$ = 3.4 Hz, $^3J(PH^B)$ = 2.7 Hz), 3.33 (s, 2 H, CH_2PdC^*), 3.51 (1 H, d, PCH, ^2J(PH) = 4.5 Hz), 4.08 (2 H, $OC\mathit{H}_2CH_3$, center of the AB part of an ABX_3 spin system); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 39.5; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 14.40 (s, $\mathit{C}H_3CH_2O$), 25.59 (d, PC, ^1J(PC) = 21.4 Hz), 28.48 (s, CH_2Pd), 33.06 (s, CH_2Pd), 58.67 (s, $\mathit{C}H_2CH_3$), 175.72 (s, C=O).

Anal. Calcd for $C_{36}H_{32}BrN_2O_2PPd_2$: C, 50.97; H, 3.80; N, 3.30. Found: C, 50.86; H, 3.93; N, 3.62.

Pd(dmba)[Ph$_2$PCHC(O)OC$_2$H$_5$] (13). To a stirred suspension of $[Pd(dmba)Cl]_2$ (1.104 g, 2 mmol) in THF (20 mL) was added at −20 °C 40 mL of solution B. Solubilization occurred, and after 0.3 h of stirring at +10 °C, pentane (100 mL) was added. White crystals of **13** developed. They were separated and recrystallized from THF/pentane (1.2 g, 58%). Suitable single crystals for X-ray diffraction were obtained from THF/pentane at 20 °C (mp 180–200 °C) (slow decomposition): IR ν(CO) + ν(CC) 1515 (vs) cm^{-1}; ^{1}H NMR (THF-d_8) δ 1.37 (3 H, t, ^3J = 7.0 Hz), 2.94 (6 H, d, $N(CH_3)_2$, ^4J(PH) = 2.0 Hz), 3.15 (1 H, d, ^2J(PH) = 0.9 Hz), 4.10 (2 H, d, NCH_2, ^4J(PH) ≃ 2 Hz), 4.18 (2 H, q, ^3J = 7.0 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 20.6; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 15.22 (s, $CH_2\mathit{C}H_3$), 49.84 (d, $(CH_3)_2N$, ^3J(PC) = 3.0 Hz), 50.84 (d, PC, ^1J(PC) = 77.8 Hz), 61.66 (s, $\mathit{C}H_2CH_3$), 71.24 (d, CH_2N, ^3J(PC)

Table I. Summary of Crystal Data and Intensity Collection of 10 and 13

compd	(dmba)Pd(μ-Cl)[μ-$Ph_2PCH(CO_2C_2H_5)$]Pd(dmba) (10)	(dmba)Pd[$Ph_2PCH(O)OC_2H_5$] (13)
formula	$C_{34}H_{40}ClN_2O_2PPd_2$	$C_{25}H_{28}NO_2PPd$
fw	787.93	511.88
cryst system	monoclinic	orthorhombic
a, Å	10.036 (4)	17.285 (5)
b, Å	34.000 (9)	17.026 (5)
c, Å	10.297 (4)	15.687 (4)
β, deg	106.82 (2)	
V, Å^3	3363	4616
Z	4	8
d(calcd), g cm^{-3}	1.556	1.476
d(obsd), g cm^{-3}	1.53 ± 0.02	1.45 ± 0.02
cryst dimens, mm	0.065 × 0.080 × 0.240	0.070 × 0.240 × 0.260
space group	$P2_1/c$ (C_{2h}^5, No. 14)	*Pbca* (D_{2h}^1, No. 61)
temp, °C	25 °C	25 °C
radiation	Mo Kα from monochromator	Mo Kα from monochromator (λ(Mo Kα_1) = 0.709 30 Å
linear abs coeff, cm^{-1}	12.08	8.82
scan speed, deg s^{-1}	0.016	0.020
scan range	1.0° + (Mo K$\alpha_1\alpha_2$ splitting)	0.9° + (Mo K$\alpha_1\alpha_2$ splitting)
2θ limits, deg	4–45	6–55
data collected	4781	4208
unique data used	2015 $I > 3\sigma(I)$	2037 $I > 3\sigma(I)$
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.075	0.056
$R_w = (\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^2)^{1/2}$	0.095	0.078
std error in an observn of unit weight	1.97e	1.63e
p fudge factor	0.08	0.08

= 3.1 Hz)8, 179.26 (d, C=O, ^2J(PC) ≃ 32 Hz).

Anal. Calcd for $C_{25}H_{28}NO_2PPd$: C, 58.66; H, 5.51; N, 2.74. Found: C, 58.71; H, 5.75; N, 2.77.

Pd(8-mq)[$Ph_2PCHC(O)OC_2H_5$] (14). To a stirred solution of **4** (0.600 g, 1.0 mmol) in THF (25 mL) was added a suspension of NaH (0.026 g, 1.08 mmol) in THF (10 mL). After 48 h of stirring at room temperature, the mixture was carefully filtered and pentane added to precipitate **14**. Recrystallization from THF/pentane afforded a pale yellow powder (0.473 g, 91%) (mp >115 °C): IR ν(CO) + ν(CC) 1508 (ssh), (ligand 8-mq) 1504 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.35 (3 H, t, ^3J = 7.2 Hz), 3.22 (2 H, d, CH_2Pd, ^3J(PH) ≃ 2 Hz), 3.31 (s, 1 H, PCH), 4.16 (2 H, q, ^3J = 7.2 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 17.0; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 15.23 (s, CH_3CH_2), 20.77 (d, CH_2Pd, ^2J(PC) = 4.6 Hz), 48.81 (d, PC, ^1J(PC) = 77.8 Hz), 61.57 (s, CH_2CH_3), 179.96 (d, C=O, ^2J(PC) = 32.5 Hz).

Anal. Calcd for $C_{26}H_{24}NO_2PPd$: C, 60.07; H, 4.65; N, 2.69. Found: C, 60.13; H, 4.79; N, 2.76.

Compound **14** could also be obtained by a procedure analogous to **13**, but this reaction proved to be less satisfactory, the compound being difficult to purify and obtained in lower yield.

Pd(dmba)(μ-Br)[μ-$Ph_2PCH(COOC_2H_5)$]Pd(8-mq) (15). To a solution of **13** (0.256 g, 0.5 mmol) in THF (20 mL) was added [Pd(8-mq)-Br]$_2$ (0.164 g, 0.25 mmol) suspended in THF (15 mL). After 12 h of stirring at room temperature the pale green solution was filtered and concentrated, and **15** was precipitated by addition of pentane, isolated as yellow-green powder, washed with pentane, and dried in vacuo (0.399 g, 95%) (mp 132–134 °C): IR ν(CO) 1674 (vs) cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ 1.19 (3 H, t, ^3J = 7.0 Hz), 2.85 (3 H, d, $CH_3{}^AN$, $^4J(PH^A)$ = 1.9 Hz), 3.03 (3 H, d, $CH_3{}^BN$, $^4J(PH^B)$ = 2.7 Hz), 3.22 (1 H, d, PCH, ^2J(PH) = 7.8 Hz), 3.37 (2 H, s, PdCH_2), δ_A 3.83 and δ_B 4.34 (2 H, ABX spin system, CH^AH^BNPdP, $^2J(H^AH^B)$ = 13.6 Hz, $J(PH^A)$ = 2.7 Hz, $J(PH^B)$ ≃ 0 Hz), 4.01 (2 H, OCH_2CH_3, center of the AB part of an ABX_3 spin system); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 50.8.

Anal. Calcd for $C_{35}H_{36}BrN_2O_2PPd_2$: C, 50.02; H, 4.32; N, 3.33. Found: C, 50.27; H, 3.97; N, 3.02.

Reaction of 13 with CO_2 To Produce 16. This reaction was performed in an NMR tube when CO_2 was bubbled through under ambient conditions into a THF-d_8 solution of **13** (0.02 M). After 15 s the signals due to **13** had completely disappeared and were replaced by those of the new compound **16**: ^{1}H NMR (THF-d_8) δ 0.94 (3 H, t, CH_3CH_2, ^3J = 7.1 Hz), 2.94 (6 H, d, $(H_3C)_2N$, ^4J(PH) = 1.9 Hz), 4.02 (2 H, q, CH_2CH_3, ^3J = 7.1 Hz), 4.07 (2 H, d, CH_2N, ^4J(PH) ≃ 1 Hz), 13.91 (≃1 H, br, OH); IR (THF) 1733 (w), 1643 (sh), 1612 (vs), 1582 (w), 1551 (s) cm^{-1}.

This reaction was shown to be reversible by bubbling pure argon into the previous solution. After 60 s the NMR signals of **16** were totally replaced by those of **13**. This experiment could be repeated for many cycles without any noticeable signs of decomposition. Attempts to isolate pure **16** in the solid state failed, even on a larger preparative scale.

Reaction of 14 with CO_2 To Prepare (8-mq)Pd[$Ph_2PC(CO_2C_2H_5)C(O)OH$] (17). This quantitative reaction was performed in the same way as the above one, but using **14** as substrate. Regeneration of **14** was observed by bubbling pure argon through a THF solution of **17**. Suitable single crystals for X-ray diffraction were obtained at −70 °C from a toluene/pentane solution: IR (THF) 1730 (w), 1651 (sh), 1613 (vs), 1578 (w), 1552 (s), 1504 (s) (ligand 8-mq) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 0.95 (3 H, t, CH_3CH_2, ^3J = 7.1 Hz), 3.12 (2 H, d, CH_2Pd, ^3J(PH) = 3.2 Hz), 4.00 (2 H, q, CH_2CH_3, ^3J = 7.1 Hz), 13.90 (1 H, br, OH).

Anal. Calcd for $C_{27}H_{24}NO_4PPd$: C, 57.51; H, 4.29; N, 2.48. Found: C, 57.44; H, 4.25; N, 2.50.

***cis*-Pt[$Ph_2PCHC(O)OC_2H_5$]$_2$ (18).** To a solution of *cis*-$PtCl_2(L^2)_2$[4] (0.404 g, 0.5 mmol) in THF (20 mL) was added a suspension of NaH (0.026 g, 1.08 mmol) in THF (10 mL). After 48 h of stirring, the solution was carefully filtered and pentane added to precipitate **18** as a beige powder. It was recrystallized from THF/pentane (0.336 g, 91%) (mp >100 °C): IR ν(CO) + ν(CC) 1518 (vs) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.31 (6 H, t, ^3J = 7.2 Hz), 3.27 (2 H, d, ^2J(PH) = 4.2 Hz), 4.10 (4 H, q, ^3J = 7.2 Hz).

Anal. Calcd for $C_{32}H_{32}O_4P_2Pt$: C, 52.10; H, 4.37. Found: C, 51.71; H, 4.20.

C. Collection of the X-ray Data and Structure Determination. The X-ray crystal and molecular structures of compounds **10** and **13** were determined by Fischer, Ricard, and Mitschler and that of compound **17** by Dusausoy.

Compounds 10 and 13. Cell constants and other pertinent data are presented in Table I. Intensity data were collected on a four-circle Philips PW1100/16 diffractometer. No intensity decay was observed during the data collection periods. It was not possible to grow a crystal of **10** with greater dimensions, and the diffraction power of this crystal was low. The raw step-scan data were converted to intensities and standard deviations by using the Lehman–Larsen algorithm.[23] The net intensities have been corrected for Lorentz and polarization factors and for absorption effects by using the Busing and Levy numerical integration.

The structures were solved on a PDP 11/60 computer using the Enraf-Nonius structure determination package[24] and the heavy-atom method. Refinements by full-matrix least squares

---

(23) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* **1974**, *A30*, 508.

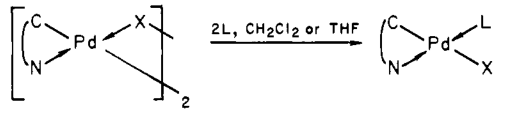
(24) Frenz, B. A. "The Enraf-Nonius CAD4 SDP. Computing in Crystallography", Schenk, H., Orthof-Hazekamp, Van Konigsveld, H., Bassi, G. C., Eds.; University Press: Delft, Holland, 1978, p 64.

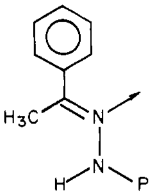
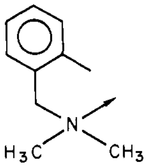
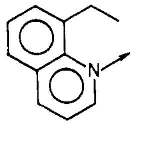
(25) Redfield, D. A.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, 10, 727–733.

Table II. Summary of Crystal Data and Intensity Collection of 17

compd	$(8\text{-mq})\mathrm{Pd}[\overline{\mathrm{Ph_2PC(CO_2C_2H_5)C(O)O}}\mathrm{H}]$ (17)
formula	$C_{27}H_{24}NO_4PPd$
fw	563.87
cryst system	triclinic
a, Å	12.206 (2)
b, Å	15.113 (2)
c, Å	15.156 (5)
α, deg	108.47 (1)
β, deg	105.36 (3)
γ, deg	99.05 (2)
V, Å^3	2461.7 (8)
Z	4
d(calcd), g cm^{-3}	1.46
cryst dimens	0.06 × 0.07 × 0.07 mm
space group	$P\bar{1}$ (C_i^1, No. 2)
temp, °C	25
radiation	Cu *K*α (λ(Cu Kα$_1$) = 1.540 51 Å)
linear abs coeff, cm^{-1}	74
scan speed	variable
scan range, deg	(1.25 + 0.14 tan θ)
2θ limits, deg	4-60°
data collected	4800
unique data used	2442$I > 2\sigma(I)$
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.070
$R_w = (\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^2)^{1/2}$	0.087
p fudge factor	0

Scheme I



	$\overline{\mathrm{C}\;\mathrm{N}}$	X	L	
	(aph)	Cl	L^2	1
	(dmba)	Cl	L^1	2
	(dmba)	Cl	L^2	3
	(8-mq)	Br	L^2	4

(all nonhydrogen atoms anisotropic) have proceeded to the *R* factor values indicated in Table II. The coordinates of the hydrogen atoms were computed with a C–H distance of 0.95 Å; their contributions were introduced in structure factor calculations. Final positional and thermal parameters for all atoms as well as a table listing the observed and calculated structure factor amplitudes of the reflections used in the refinement are available as supplementary material.[22]

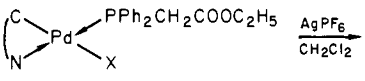
Compound 17. Cell constants and other pertinent data are presented in Table II. Intensity data were collected on a Nonius CAD 4 diffractometer. No intensity decay was observed during the data collection periods. It was not possible to obtain better diffracting crystals, and the quality of the structure determination is given by *R*, R_W Table II), and the σ values (Table VII). Absorption corrections were omitted in view of the low linear absorption coefficient. The structure were solved by Patterson and Fourier methods. Refinements by full-matrix least squares (all nonhydrogen atoms anisotropic) have proceeded to the R factor values indicated in Table II, using the Shel X[21] method. Final positional and thermal parameters for all atoms as well as a table listing the observed and calculated structure factor amplitudes of the reflections used in the refinement are available as supplementary material.[22]

Results and Discussion

Complexes with Ph_2PCH_2Y (Y = CN, $COOC_2H_5$). The neutral palladium complexes with L^1 or L^2 were obtained in good yields (see Experimental Section) by reacting the cyclometalated $[(\overline{\mathrm{C}\;\mathrm{N}})PdX]_2$ complexes with a stoichiometric amount of ligand (Scheme I). Bridge cleavage occurs easily, and for the resulting complexes 1-4, the spectroscopic data (IR, NMR) indicate that the function Y does not interact with the metal and that the halogen is always found trans with respect to the σ-bonded C atom, which is in agreement with the reluctance of phosphines to bind in this position. This has already been found in related complexes.[20]

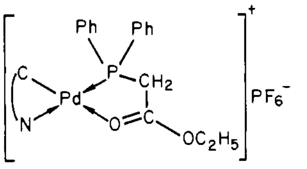
From these and previous[4] investigations it can be deduced that when Ll^1 and L^2 act as monodentate ligands, their coordinating power is very similar to PPh_3. Their main interest is to be found in their chelating or bridging ability and in the facilitated CH cleavage in the position α to the coordinated phosphorus. These points will be discussed later (vide infra).

In complexes **5** and **6**, obtained according to eq 1, the CO stretching frequencies at 1651 and 1628 cm^{-1}, respectively, accounted for the chelating behavior of the phosphine ester. Their difference is related to a Pd(II) less electron deficient in **5** than in **6**, requiring less electron donation from the ester function.



3, $\overline{\mathrm{C}\;\mathrm{N}}$ = dmba, X = Cl

4, $\overline{\mathrm{C}\;\mathrm{N}}$ = 8-mq, X = Br



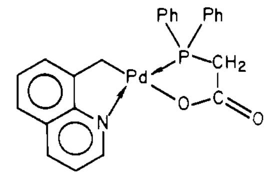
(1)

5

6

As for **3** and **4**, the phosphorus atom binds trans to nitrogen in **5** and **6**. This is easily deduced from the observation of the coupling constant of $N(CH_3)_2$ protons with phosphorus in **5** (^4J(PH) = 2.9 Hz). For both compounds **5** and **6** a high-field shift of ca. 5 ppm of the ^{31}P NMR signal has occurred when compared to the corresponding shifts for **3** and **4**.

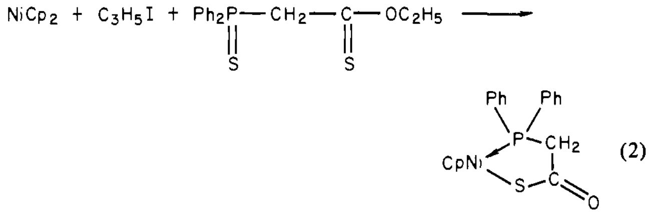
Shaw and et al. have shown that similar phosphine ester ligands can undergo base-promoted O-metallation with loss of the C_2H_5 group. We have also observed such a reaction from (8-mq)Pd(Br)L^2 in the presence of BuLi in THF, leading to[26]



A further example of dealkylation is given in eq 2,[27] from which

---

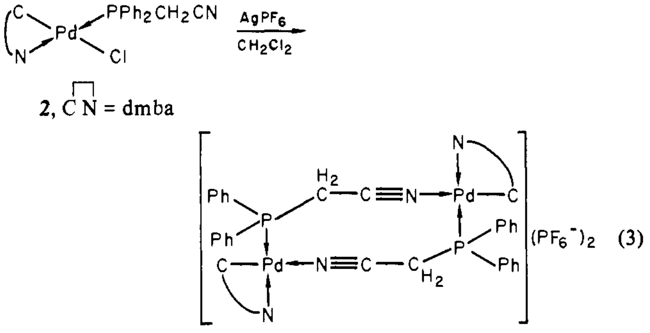
[26] This was a byproduct observed in variable quantities in the reaction of $[(8\text{-mq})PdBr]_2$ with solution B, when a slight excess of BuLi was present (coming from the lithium amide synthesis). We have checked that this compound does not result from reaction of **4** with the amide but with BuLi.



(2)

we expected the obtention of a nickel(II)-phosphine thioester complex, potential[4] precursor of $Ph_2PCH_2C(S)OC_2H_5$. Instead, S-metalation and dealkylation occur, related to the affinity of nickel for sulfur.

With L^1 on the other hand, chelation of the ligand was never observed because of the constraint imposed by the nitrile group. Bridge formation occurred in **7**, prepared according to eq 3. In spite of the low solubility of **7** in usual organic solvents, its ^1H NMR spectrum shows that the phosphorus atom is still coordinated trans to nitrogen ($^4J(PH) = 2.9$ Hz). The increase of the $\nu(CN)$ frequency (2298 cm^{-1}) when compared with the value in the free ligand (2240 cm^{-1}) indicates a σ coordination of the $-C{\equiv}N$ function through the nitrogen. We therefore suggest for **7** the binuclear structure depicted above.



2, C͡N = dmba

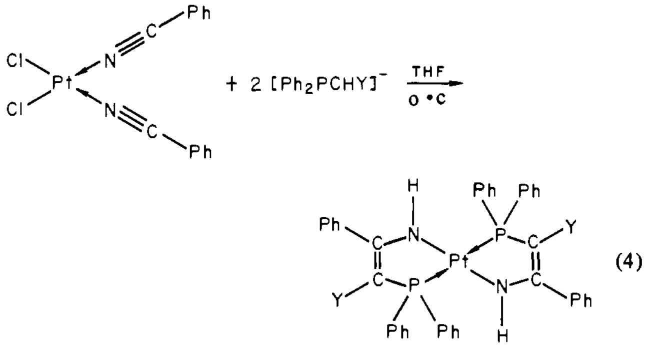
(3)

7

Complexes with $[Ph_2PCHY]^-$ ($Y = CN, COOC_2H_5$). These ligands can be prepared by reacting $LiN(c\text{-}C_6H_{11})(i\text{-}Pr)$ at -5 °C with a THF solution of L^1 or L^2. Whereas the carbanion $[L^1]^-$ has previously been used in the Wittig reaction,[28] $[L^2]^-$ had not yet been reported. Beside the carbanions themselves, each of their solutions (solution A for Y = CN; solution B for $Y = COOC_2H_5$) contained variable amounts of the corresponding phosphine (ca. 20%, see Experimental Section). This explains the isolation in each of the following reactions of secondary products with neutral ligands L^1 or L^2. These complexes have been described above and will not be further discussed.

In view of the known lability of the nitrile ligand in $PtCl_2(PhCN)_2$, this complex was a good candidate for the preparation of the Pt–P–C triangular species by reaction with $[L^1]^-$ or $[L^2]^-$. Such units should indeed present a very interesting reactivity.[29,30] Surprisingly, nucleophilic attack occurs at the coordinated nitrile and not at the metal center (eq 4), leading to a bis five-membered ring structure and presenting what appeared to be the first reaction of a carbanion with a coordinated nitrile.[11]

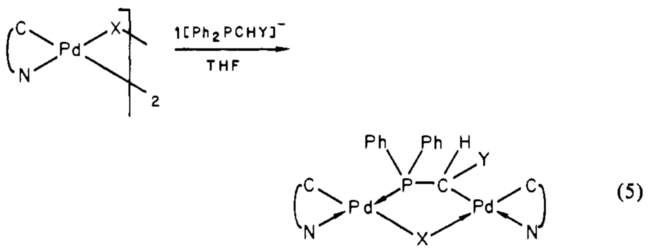
In reaction 4 the four ligands around the platinum contribute to the formation of the new compound. In order to restrain the reaction possibilities with the functional carbanions, we decided to investigate the reactivity of cyclometalated Pd(II) complexes toward L^-. In these complexes, the organometallic chelating ligand (dmba or 8-mq) was not expected to react with the carbanion, leaving therefore only two potential reactive coordination sites.



(4)

Y = CN, COOC$_2$H$_5$

Addition of 1 equiv of L^- to $[(\text{C͡N})PdX]_2$ in THF (eq 5) led to the binuclear Pd(II) complexes **8**, **10**, **11**, and **12**. It is easily deduced from their IR spectra that the Y functions do not take part in the bonding to the metals ($\nu(C{=}O) = 1672$ and 1672 cm^{-1} for **10** and **12**; $\nu(C{\equiv}N) = 2192$ and 2173 cm^{-1} for **8** and **11**, respectively). The presence of the single resonance in the ^{31}P NMR spectrum excludes the existence of different isomers. The chirality of the C* atom in the bridge induces inequivalence of the OCH_2 protons, giving for the ethyl protons in complexes **10** and **12** an ABX_3 spin system. Because of their geometry the two different bridging groups between the metals give rise to nonequivalence for the two Pd(C͡N) moieties. The ^1H and ^{13}C NMR spectra of **8** andd **10** clearly showed the inequivalence of the four N-methyl groups. The occurrences of an ABX pattern (X = P) for the CH_2NPdP protons and of an AB pattern for the CH_2NPdC^* protons are further evidence for the lack of symmetry in the molecules. The observation of $^4J(P\text{–}H)$ coupling constants for one Pd(C͡N) moiety indicates a trans NPdP arrangement as found, e.g., in **5**. This was confirmed by the X-ray structure determination of **10** and is also suggested for complexes **11** and **12**.



(5)

8, C͡N = dmba, X = Cl, Y = CN

10, C͡N = dmba, X = Cl, Y = COOC$_2$H$_5$

11, C͡N = 8-mq, X = Br, Y = CN

12, C͡N = 8-mq, X = Br, Y = COOC$_2$H$_5$

The molecular structure of **10** is shown in Figure 1. Crystal data are given in Table I, the interatomic distances and angles in Table III, and least-squares planes in Table IV. From the stereoview of the molecule (Figure 2) one clearly sees its folding along the Cl–C(13) axis, the angles between the two square planes being 36.3°. The Pd(1)–Pd(2) distance (3.88 Å) is too long for any metal–metal interaction. Similarly no interaction is to be found between the ester function and the metals. The three fused metallacycles are puckered, and their distorsion angles are given in Table VI. The Pd–Cl distances (average 2.43 Å) are consistent with a bridging Cl trans with respect to C(17) and C(26). The $Ph_2PCHCOOC_2H_5$ bridging unit deserves some comments. The three P–C(1), P–C(7), and P–C(13) distances are equivalent, and thus no double-bond character is to be found in the P–C(13) bond.

---

(27) Synthesis of $CpNi[Ph_2PCH_2C(O)S]$: a toluene solution of $Ph_2P(S)CH_2C(S)OC_2H_5$ (6.4 g, 20 mmol), $NiCp_2$ (9.44 g, 50 mmol), and C_3H_5I (3.36 g, 20 mmol) was refluxed for 7 h. This mixture was then chromatographed on a silica gel column (eluting with toluene) and afforded $CpNi[Ph_2PCH_2C(O)S]$ (4.0 g): mp >180 °C; mass spectrum, m/e 382 (M^+), IR (KBr) $\nu(CO)$ 1622 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.53 (2 H, d, PCH_2, $^2J(PH) = 10.6$ Hz), 5.33 (s, C_5H_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 20.6.

(28) Reetz, M. T.; Eibach, F. *Justus Liebigs Ann. Chem.* **1977**, 242–253.

(29) Karsch, H. H. *Chem. Ber.* **1977**, 2213–2221.

(30) Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272–3273.

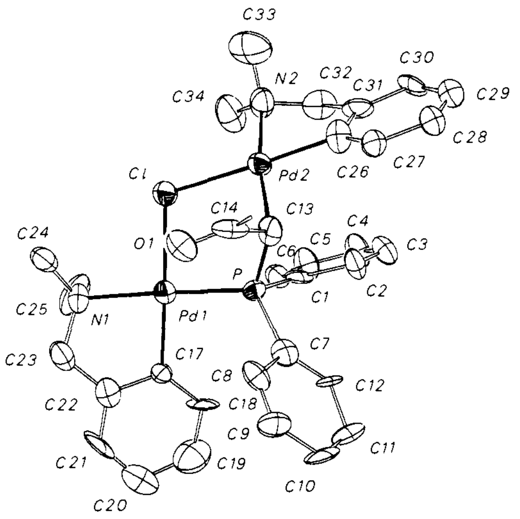


Figure 1. The molecular structure of compound **10**. The ethoxy group on C(14) has been omitted for clarity.

Table III. Selected Interatomic Distances (Å) and Angles (Deg) in Pd(dmba)(μ-Cl)[μ-Ph$_2$PCH(COOC$_2$H$_5$)]Pd(dmba) (**10**)

Pd(1)–N(1)	2.15 (1)	C(21)–C(22)	1.37 (3)
Pd(1)–C(17)	2.03 (2)	N(2)–C(34)	1.38 (3)
Pd(1)–P	2.233 (6)	N(2)–C(33)	1.42 (3)
Pd(1)–Cl	2.421 (6)	N(2)–C(32)	1.47 (3)
Pd(2)–Cl	2.445 (5)	C(32)–C(31)	1.51 (3)
Pd(2)–C(13)	2.01 (2)	C(31)–C(26)	1.35 (3)
Pd(2)–N(2)	2.15 (2)	C(26)–C(27)	1.38 (3)
Pd(2)–C(26)	2.00 (2)	C(27)–C(28)	1.42 (3)
P–C(1)	1.82 (2)	C(28)–C(29)	1.40 (3)
P–C(7)	1.85 (2)	C(29)–C(30)	1.40 (3)
P–C(13)	1.81 (2)	C(30)–C(31)	1.41 (3)
C(13)–C(14)	1.52 (3)	C(1)–C(2)	1.41 (2)
C(14)–O(1)	1.15 (2)	C(2)–C(3)	1.40 (2)
C(14)–O(2)	1.39 (2)	C(3)–C(4)	1.39 (3)
O(2)–C(15)	1.40 (2)	C(4)–C(5)	1.36 (3)
C(15)–C(16)	1.35 (3)	C(5)–C(6)	1.37 (3)
N(1)–C(24)	1.40 (2)	C(6)–C(1)	1.39 (3)
N(1)–C(25)	1.48 (2)	C(7)–C(8)	1.38 (3)
N(1)–C(23)	1.53 (2)	C(8)–C(9)	1.33 (3)
C(23)–C(22)	1.46 (3)	C(9)–C(10)	1.39 (3)
C(22)–C(17)	1.38 (2)	C(10)–C(11)	1.37 (3)
C(17)–C(18)	1.32 (3)	C(11)–C(12)	1.44 (3)
C(18)–C(19)	1.38 (3)	C(7)–C(12)	1.36 (3)
C(19)–C(20)	1.40 (3)	Pd(2)–H(13)	2.52
C(20)–C(21)	1.37 (3)		
N(1)–Pd(1)–P	173.8 (5)	Pd(1)–P–C(13)	111.6 (6)
N(1)–Pd(1)–Cl	94.3 (5)	P–C(13)–Pd(2)	105 (1)
N(1)–Pd(1)–C(17)	81.1 (7)	P–C(13)–C(14)	112 (1)
Cl–Pd(1)–P	88.8 (2)	Pd(1)–Cl–Pd(2)	105.9 (2)
Cl–Pd(1)–C(17)	168.9 (6)	Pd(2)–N(2)–C(32)	101 (1)
P–Pd(1)–C(17)	96.6 (5)	N(2)–C(32)–C(31)	109 (2)
N(2)–Pd(2)–Cl	94.1 (5)	C(32)–C(31)–C(26)	117 (2)
N(2)–Pd(2)–C(13)	168.5 (7)	C(31)–C(26)–Pd(2)	112 (1)
N(2)–Pd(2)–C(26)	82.1 (9)	C(27)–C(26)–Pd(2)	127 (1)
C(13)–Pd(2)–Cl	91.1 (6)	Pd(1)–P–C(1)	112.5 (6)
C(13)–Pd(2)–C(26)	92.4 (9)	Pd(1)–P–C(7)	117.7 (7)
Cl–Pd(2)–C(26)	176.2 (8)	Pd(1)–P–C(13)	111.6 (6)
Pd(1)–N(1)–C(23)	104 (1)	C(13)–P–C(1)	102.1 (9)
N(1)–C(23)–C(22)	108 (2)	C(13)–P–C(7)	104.8 (9)
C(23)–C(21)–C(17)	60.7 (9)	C(1)–P–C(7)	106.4 (9)
C(22)–C(17)–Pd(1)	112 (1)		

This contrasts with the bridging Me$_2$PCH$_2$ anion in (Me$_3$P)$_2$Co(μ-PMe$_2$)(μ-CH$_2$PMe$_2$)Co(PMe$_3$)$_2$ for which the P–CH$_2$ distance (1.71 (1) Å) is perceptibly shorter than the PMe distances (average 1.83).[31] The Pd(1)–C(17) (2.03 Å), Pd(2)–C(13) (2.01 Å), and Pd(2)–C(26) (2.00 Å) distances are in the normal range for Pd–C σ bonds. It seems difficult to find any obvious correlation between the ^{1}H, ^{13}C, and ^{31}P NMR data reported in the experimental part. Nevertheless they allow us together with the IR data to propose with confidence that complexes **8**, **11**, and **12** have a structure analogous to that of **10**.

Table IV. Least-Squares Planes for Pd(dmba)(μ-Cl)[μ-Ph$_2$PCH(COOC$_2$H$_5$)]Pd(dmba) (10)

plane No.	atoms	dist from plane, Å
1	Pd(1)	0.002 (2)
	Pd(2)	−0.003 (2)
	P	−0.060 (6)
	C(13)	0.937 (21)
	Cl[a]	0.053 (7)
2	Pd(1)	0.001 (2)
	Cl	−0.022 (7)
	P	0.019 (6)
	N(1)	0.185 (18)
	C(17)	−0.318 (23)
3	Pd(1)	0.002 (2)
	C(17)	−0.187 (23)
	C(22)	0.004 (25)
	C(23)	0.380 (25)
	N(1)	−0.228 (18)
4	C(17)	0.005 (23)
	C(18)	−0.001 (27)
	C(19)	−0.018 (34)
	C(20)	0.026 (32)
	C(21)	−0.014 (28)
	C(22)	0.000 (26)
5	Pd(2)	0.003 (2)
	Cl	−0.002 (7)
	C(13)	−0.212 (24)
	C(26)	−0.018 (26)
	N(2)	−0.148 (21)
	C(32)[a]	−0.960 (28)
6	C(26)	−0.016 (28)
	C(27)	0.012 (25)
	C(28)	0.011 (27)
	C(29)	−0.036 (28)
	C(30)	0.027 (24)
	C(31)	0.006 (25)
7	Cl	−0.038 (7)
	Pd(1)	0.005 (2)
	P	−0.086 (6)
	C(13)	0.850 (21)

Dihedral Angles between the Planes

plane	angle, deg	plane	angle, deg
1–5	34.0	2–5	36.3
2–4	27.9	5–6	22.3

Equations of the Planes of the Form $Ax + By + Cz - D = 0$

plane	A	B	C	D
1	−0.1793	0.1693	−0.9691	2.4870
2	−0.2149	0.1379	0.9669	2.6692
3	−0.4020	0.0481	−0.9144	−3.2549
4	−0.5734	−0.1413	−0.8070	3.8554
5	−0.0177	0.6801	−0.7329	−1.6453
6	0.1109	0.8932	−0.4358	−4.1521
7	−0.1672	0.1313	−0.9771	−2.6164

[a] This atom was not used in defining the plane.

We are aware of only few reports in the literature concerning the direct reaction of [R$_2$PCH$_2$]$^-$ (R = CH$_3$,[32,33] R = Ph[34]) with transition metals. Although the detailed mechanism of our reaction is not known with certainty, we believe that the incorporation of the Ph$_2$PCHY-bridging unit occurs via a mononuclear

---

[31] Klein, H. F.; Wenninger, J.; Schubert, U. *Z. Naturforsch., B*: *Anorg. Chem., Org. Chem.* **1979**, *34b*, 1391–1397.

[32] Karsch, H. H.; Schmidbaur, H. *Z. Naturforsch. B*: *Anorg. Chem., Org. Chem.* **1977**, *32b*, 762–767.

[33] Schmidbaur, H.; Blaschke, G. *Z. Naturforsch., B*: *Anorg. Chem. Org. Chem.* **1980**, *35*, 584–587.

[34] Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251–4253.

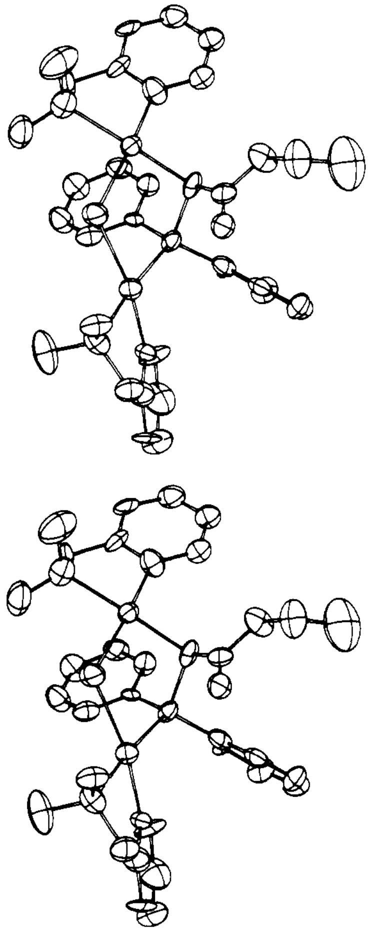


Figure 2. A stereoscopic view of compound **10**.

Table V. Selected Interatomic Distances (Å) and Angles (Deg) in Pd(dmba)($Ph_2PCHC(O)OC_2H_5$) (**13**)

Pd-P	2.242 (2)	C(3)-C(4)	1.39 (1)
Pd-C(1)	1.973 (7)	C(4)-C(5)	1.35 (1)
Pd-N	2.119 (6)	C(5)-C(6)	1.39 (1)
Pd-O(1)	2.117 (5)	C(6)-C(1)	1.39 (1)
P-C(10)	1.751 (9)	C(6)-C(7)	1.55 (1)
P-C(14)	1.822 (8)	C(14)-C(15)	1.39 (1)
P-C(20)	1.830 (8)	C(15)-C(16)	1.38 (1)
C(10)-C(11)	1.37 (1)	C(16)-C(17)	1.39 (1)
C(11)-O(1)	1.27 (1)	C(17)-C(18)	1.40 (1)
C(11)-O(2)	1.36 (1)	C(18)-C(19)	1.37 (1)
C(12)-O(2)	1.44 (1)	C(19)-C(14)	1.40 (1)
C(12)-C(13)	1.48 (1)	C(20)-C(21)	1.38 (1)
N-C(7)	1.45 (1)	C(21)-C(22)	1.37 (1)
N-C(8)	1.48 (1)	C(22)-C(23)	1.36 (1)
N-C(9)	1.48 (1)	C(23)-C(24)	1.40 (1)
C(1)-C(2)	1.39 (1)	C(24)-C(25)	1.39 (1)
C(2)-C(3)	1.41 (1)	C(25)-C(20)	1.39 (1)
O(1)-Pd-N	91.6 (2)	O(1)-C(11)-C(10)	126.8 (9)
O(1)-Pd-C(1)	174.1 (2)	O(1)-C(11)-O(2)	115.6 (8)
O(1)-Pd-P	83.8 (1)	C(10)-C(11)-O(2)	117.4 (9)
P-Pd-C(1)	102.1 (2)	P-C(10)-C(11)	114.2 (7)
P-Pd-N	174.5 (2)	Pd-N-C(7)	107.5 (5)
C(1)-Pd-N	82.4 (3)	Pd-N-C(8)	107.2 (4)
Pd-P-C(10)	100.5 (3)	Pd-N-C(9)	113.2 (5)
Pd-P-C(14)	119.7 (3)	C(8)-N-C(9)	110.3 (6)
Pd-P-C(20)	115.0 (2)	N-C(7)-C(6)	109.6 (7)
C(10)-P-C(14)	109.0 (4)	C(7)-C(6)-C(1)	116.0 (7)
C(10)-P-C(20)	108.5 (4)	C(6)-C(1)-Pd	113.6 (6)
C(14)-P-C(20)	103.6 (3)	C(2)-C(1)-Pd	129.1 (6)

Table VI. Least-Squares Planes for Pd(dmba)($Ph_2PCHC(O)OC_2H_5$) (**13**)

plane No.	atoms	dist from plane, Å
1	Pd	0.002 (1)
	P	−0.009 (2)
	O(1)	0.004 (6)
	N	−0.098 (8)
	C(1)	−0.003 (9)
2	Pd	0.000 (1)
	P	0.000 (2)
	C(10)	−0.014 (9)
	C(11)	0.028 (10)
	O(1)	−0.009 (6)
3	Pd	0.001 (1)
	N	−0.190 (8)
	C(1)	−0.131 (9)
	C(6)	−0.018 (10)
	C(7)	0.360 (11)
4	C(1)	0.006 (9)
	C(2)	−0.009 (10)
	C(3)	0.006 (11)
	C(4)	0.001 (11)
	C(5)	−0.003 (11)
	C(6)	−0.001 (10)
5	Pd	0.000
	P	0.000
	C(10)	0.000
6	Pd	0.000 (1)
	O(1)	−0.009 (6)
	C(11)	0.028 (10)
	C(10)	−0.013 (9)

Dihedral Angles between the Planes

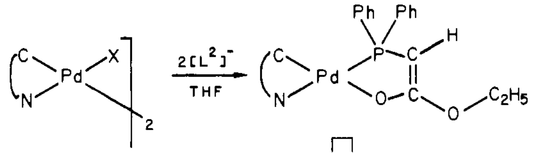
plane	angle, deg	plane	angle, deg
2-3	4.3	3-4	10.3

Equations of the Planes of the Form $Ax + By + Cz - D = 0$

plane	A	B	C	D
1	0.6322	0.6443	−0.4303	3.6667
2	0.6367	0.6384	−0.4326	−3.6672
3	0.5849	0.6490	−0.4866	−3.4604
4	0.6765	0.5031	−0.5379	3.4554
5	0.6305	0.6428	−0.4350	3.6545
6	0.6368	0.6380	−0.4329	3.6666

intermediate (vide infra). Nevertheless this reaction appears to be the first example of the direct formation from the free carbanion of bimetallic complexes containing a MPCM unit. Previously reported formations of such units resulted from C-H bond activation of neutral ligands in mono- or polynuclear systems[31,35-37] or from stepwise buildup.[34]

Addition of 2 equiv of $[L^2]^-$ to $[(\overline{C\ N})PdX]_2$ gave as the only product a mononuclear Pd(II) complex (eq 6) in which the



(6)

13, $\overline{C\ N}$ = dmba, X = Cl

14, $\overline{C\ N}$ = 8-mq, X = Br

functional carbanion behaves now as a chelating ligand. This was shown by the presence of a strong IR absorption at ca. 1510 cm^{-1} ($\nu(C\dashv O) + \nu(C\dashv C)$).

The trans N-Pd-P arrangement in **13** follows from the ^4J(PH) values ($^4J(P\text{-}H_3CN)$ = 2 Hz, $^4J(P\text{-}H_2CN)$ = 2 Hz). The increase of ^1J(PC) (77.8 Hz for both complexes) when compared with cationic **5** and **6** (33.3 and 31.4 Hz) is attributed to the change in hybridization of the α-carbon atom from sp^3 in the neutral

---

(35) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2727–2730.

(36) Cotton, F. A.; Frenz, B. A.; Hunter, D. L. *J. Chem. Soc., Chem. Commun.*, **1974**, 755–756.

(37) Bonnet, J. J.; Lavigne, G.; Lugan, N. *Proc. Int. Conf. Coord. Chem., 21st* **1980**, *Abstract No. 325.*

(38) Mutet, C.; Pfeffer, M. *J. Organomet. Chem.* **1979**, *171*, C34–C36.

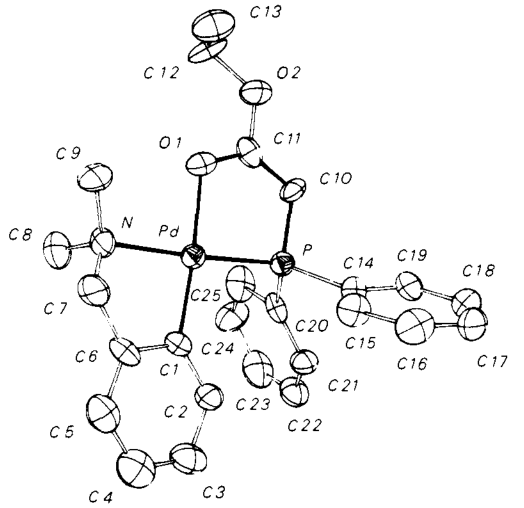
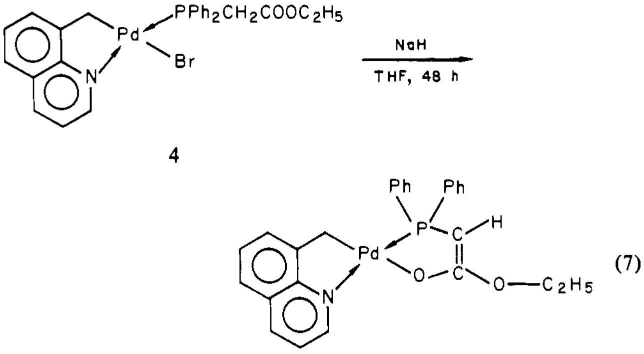


Figure 3. The molecular structure of compound 13.

chelate to sp^2 in the carbanionic one. Also to be noted are the low values of ^2J(PH) (<1 Hz). For the synthesis fo **14**, we have found some difficulties with reaction 6 and have achieved a direct synthesis (91% yield) from the easily available **4** by using NaH (eq 7). The molecular structure of **13** was determined by X-ray

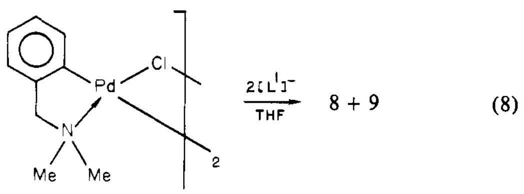


4

(7)

14

diffraction and is depicted in Figure 3. Crystal data are given in Table I, interatomic distances and angles in Table V, and least-squares planes in Table VI. The palladium has a square-planar environment with an angle between the planes of the two five-membered rings of 4.3°. The electron delocalization withing the $\overline{\mathrm{P\ O}}$ chelate is shown by the P–C(10) distance (1.751 (9) Å), shorter than the P–C(14) and P–C(20) (average 1.826 (8) Å) bonds, by the short C(10)–C(11) distance (1.37 (1) Å), and by the C(11)–O(1) distance (1.27 (1) Å) intermediate between that in the free ligand (1.15 (2) Å) as in **10**, and that of C(11)–O(2) (1.36 (1) Å). Other distances and angles within the molecule are normal. This structure shows that [L^2]$^-$ prefers to form a stable five-membered ring when possible instead of an MPC triangle. Even on reacting [Pd(dmba)Cl]$_2$ with 2 equiv of [L^1]$^-$, such a structural unit was not observed. We isolated instead (eq 8)



(8)

complex **8** already obtained (eq 5) when using a [Pd]/[L^1]$^-$ ratio of 2/1. **8** might well result from the reaction of the mononuclear [(dmba)Pd(Ph$_2$PCHCN)] with [(dmba)PdCl]$_2$. This mononuclear intermediate seems too reactive to be isolated, whereas its homologous **13** is stabilized and was indeed shown to be the intermediate in the synthesis of **8** (vide infra, eq 9). Besides **8**, the soluble complex **9** could be isolated in variable amounts (20–30%). Because of unsatisfactory microanalytical data, **9** could not be unambigously identified. Spectroscopic data (see Experimental Section) suggested that **9** has resulted from reaction of [L^1]$^-$ with coordinated Ph$_2$PCH$_2$CN always present in the reaction mixture.

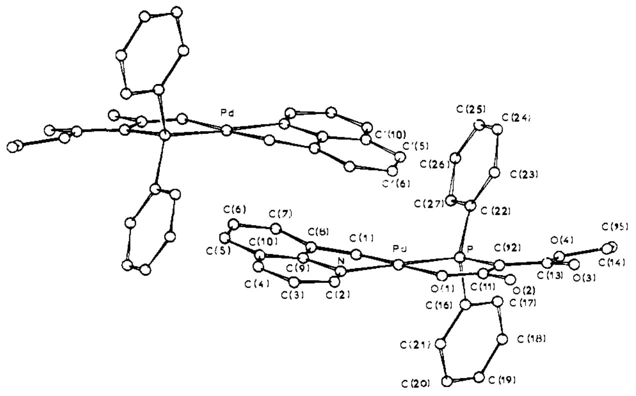
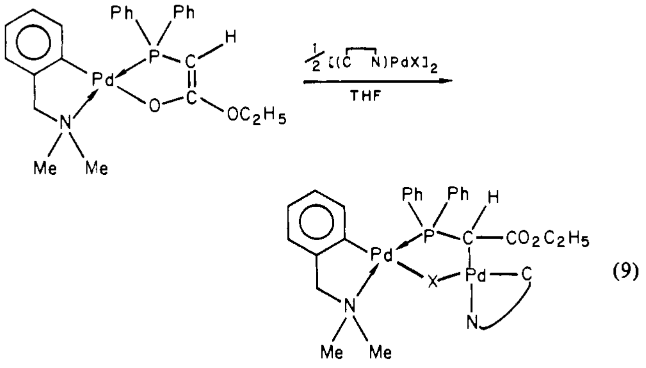


Figure 4. A view of the structure of two molecules of **17** constituting a centrosymmetric "dimer".

The reactivity of **13** is based on the nucleophilic character of C(10). As briefly mentioned above, we could establish[1] that **13** is in fact the first compound to be formed in reaction 5. It further reacts with the remaining [($\overline{\mathrm{C\ N}}$)PdX]$_2$, forming **8**. This was confirmed and extended by performing eq 9. This high-yield mild



(9)

10, ($\overline{\mathrm{C\ N}}$) = dmba, X = Cl

15, ($\overline{\mathrm{C\ N}}$) = 8-mq, X = Br

reaction represents a potential useful access to dissymmetric bimetallic species. We are currently investigating these possibilities.

Reactions with CO$_2$. The most interesting property of **13** and **14** is to be found in their reaction with CO$_2$. Bubbling dry CO$_2$ under ambient conditions into an NMR tube of a THF-d_8 solution of **13** or **14** in a few seconds causes the complete disappearance of the ^{1}H NMR signals of the P–C*H* proton. A new signal at ca. 13.9 ppm appears, which is assigned to an enolic OH proton. This proton exchanges with D$_2$O. The reaction is totally reversible when argon is bubbled through the solution (see Experimental Section), and this cycle can be reproduced several times. Attempts to isolate in the solid state the pure reaction product **16** of **13** with CO$_2$ failed: only mixtures of **13** and **16** were obtained as indicated by the IR spectra. Although these attempts where performed under CO$_2$, addition of pentane to a THF solution containing pure **16** (controlled by NMR) only afforded **13** by slow crystallization. Similarly, a toluene solution of **14** was bubbled with CO$_2$ but addition of pentane induced here the crystallization of the new complex **17** (see Experimental Section). The molecular structure of this compound is shown in Figure 4.

Crystal data are given in Table II, interatomic distances and angles in Table VII, and least-squares planes in Table VIII. The asymmetric unit consists of two slightly different molecules. Each of them is associated to a second molecule deduced by a center of symmetry. These couples of molecules will be referred to as

Table VII. Selected Interatomic Distances (Å) and Angles (Deg) in (8-mq)$\overline{\text{Pd[Ph}_2\text{PC(CO}_2\text{C}_2\text{H}_5\text{)C(O}}$)OH] (**17**)

bond	"dimer" 1	"dimer" 2
Pd–P	2.207 (8)	2.226 (6)
Pd–O(1)	2.16 (2)	2.15 (2)
Pd–N	2.06 (3)	2.08 (2)
Pd–C(1)	2.05 (2)	2.04 (2)
C(1)–C(8)	1.50 (3)	1.48 (3)
C(8)–C(9)	1.42 (3)	1.45 (3)
C(9)–N	1.40 (3)	1.36 (3)
N–C(2)	1.32 (3)	1.38 (3)
C(2)–C(3)	1.43 (4)	1.42 (3)
C(3)–C(4)	1.40 (4)	1.34 (3)
C(4)–C(10)	1.36 (4)	1.44 (3)
C(10)–C(9)	1.45 (3)	1.40 (3)
C(10)–C(5)	1.47 (4)	1.42 (3)
C(5)–C(6)	1.33 (4)	1.37 (3)
C(6)–C(7)	1.41 (4)	1.47 (3)
C(7)–C(8)	1.41 (3)	1.37 (3)
P–C(12)	1.80 (3)	1.79 (2)
C(12)–C(11)	1.40 (3)	1.46 (3)
C(11)–O(1)	1.25 (3)	1.22 (2)
C(11)–O(2)	1.34 (3)	1.35 (3)
C(12)–C(13)	1.45 (3)	1.38 (3)
C(13)–O(3)	1.20 (3)	1.26 (3)
C(13)–O(4)	1.37 (3)	1.37 (2)
O(4)–C(14)	1.47 (3)	1.46 (3)
C(14)–C(15)	1.54 (4)	1.56 (3)
P–C(16)	1.85 (2)	1.84 (2)
P–C(22)	1.84 (2)	1.81 (2)
O(3)–O(2)	2.56 (2)	2.48 (2)
Pd–C(21)	3.51 (2)	3.56 (2)
Pd–H(21)	2.87	
Pd–C′(5)	3.35 (2)	3.38 (2)
Pd–C′(6)	3.58 (2)	
Pd–C′(10)		3.70 (2)
Pd–H′(5)	3.45	
P–Pd–O(1)	84.6 (5)	84.8 (5)
O(1)–Pd–N	95.8 (8)	95.3 (7)
N–Pd–C(1)	83.7 (10)	83.3 (8)
C(1)–Pd–P	96.0 (7)	96.7 (7)
Pd–P–C(12)	99.6 (10)	100.7 (7)
Pd–P–C(22)	116.2 (7)	116.2 (7)
Pd–P–C(16)	113.3 (10)	116.8 (7)
C(16)–P–C(22)	107 (1)	106 (1)
P–C(12)–C(11)	116 (2)	112 (2)
C(12)–C(11)–O(1)	124 (3)	127 (2)
C(12)–C(11)–O(2)	120 (3)	116 (2)
C(11)–O(1)–Pd	116 (2)	115 (1)
P–C(12)–C(13)	125 (2)	128 (2)
C(11)–C(12)–C(13)	119 (3)	120 (2)
C(12)–C(13)–O(3)	126 (3)	126 (2)
C(12)–C(13)–O(4)	113 (3)	115 (2)
C(13)–O(4)–C(14)	117 (2)	115 (2)
O(4)–C(14)–C(15)	106 (2)	106 (2)
Pd–C(1)–C(8)	107 (2)	109 (1)
C(1)–C(8)–C(9)	119 (2)	117 (2)
C(8)–C(9)–N	115 (3)	116 (2)
C(9)–N–Pd	113 (2)	113 (1)
C(9)–N–C(2)	116 (3)	119 (2)
N–C(2)–C(3)	128 (3)	119 (2)
C(2)–C(3)–C(4)	112 (3)	117 (2)
C(3)–C(4)–C(10)	126 (3)	117 (2)
C(4)–C(10)–C(9)	116 (3)	119 (2)
C(4)–C(10)–C(5)	130 (3)	121 (2)
C(10)–C(9)–C(8)	124 (2)	122 (2)
C(10)–C(9)–N	122 (3)	122 (2)
C(10)–C(5)–C(6)	123 (3)	119 (2)
C(5)–C(6)–C(7)	123 (3)	121 (2)
C(6)–C(7)–C(8)	119 (3)	121 (2)
C(7)–C(8)–C(1)	123 (3)	125 (2)
C(7)–C(8)–C(9)	118 (2)	117 (2)

Table VIII. Least-Squares Planes for (8-mq)$\overline{\text{Pd[Ph}_2\text{PC(CO}_2\text{C}_2\text{H}_5\text{)C(O}}$)OH] (**17**)

planes	atoms	distances from plane, Å
1	Pd	−0.02 (0)
	P	0.02 (1)
	N	0.02 (2)
	C(1)	−0.01 (3)
	O(1)	−0.01 (2)
2	N	−0.07 (2)
	C(1)	0.07 (3)
	C(2)	−0.07 (3)
	C(3)	0.01 (3)
	C(4)	0.04 (3)
	C(5)	0.05 (3)
	C(6)	−0.05 (3)
	C(7)	−0.06 (3)
	C(8)	0.01 (3)
	C(9)	0.01 (3)
	C(10)	0.06 (3)
3	Pd	−0.02 (0)
	O(1)	0.02 (2)
	C(11)	0.01 (3)
	O(2)	0.01 (2)
	C(12)	0.01 (3)
	C(13)	0.00 (3)
	C(14)	−0.12 (3)
	C(15)	0.10 (3)
	O(3)	−0.12 (2)
	O(4)	0.04 (2)
	P	0.06 (1)
4	Pd	−0.02 (0)
	O(1)	0.02 (2)
	C(11)	−0.01 (3)
	C(12)	−0.03 (3)
	P	0.03 (1)
5	C(16)	0.00 (3)
	C(17)	−0.01 (3)
	C(18)	0.01 (3)
	C(19)	0.00 (3)
	C(20)	−0.01 (3)
	C(21)	0.01 (3)
6	C(22)	0.00 (3)
	C(23)	−0.03 (3)
	C(24)	0.03 (3)
	C(25)	−0.03 (3)
	C(26)	0.02 (3)
	C(27)	0.00 (3)

Dihedral Angles between the Planes

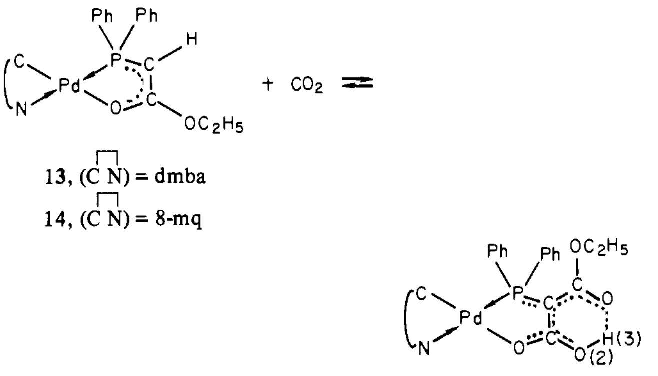
planes	angle, deg	planes	angle, deg
1–2	13	4–5	103
3–4	2.2	4–6	112

Equations of the Planes of the Form $Ax + By + Cz - D = 0$

plane	A	B	C	D
1	−0.026 48	0.014 14	−0.001 37	0.015 69
2	−0.124 36	0.084 97	0.024 43	0.346 26
3	−5.099 31	2.570 72	−0.355 37	2.682 94
4	−5.054 63	2.664 96	0.350 99	2.410 21
5	0.426 07	0.115 37	1.780 62	9.337 63
6	1.326 14	1.102 55	0.431 41	3.088 44

"dimer 1" and "dimer 2" in Table VII.

The reaction occurs by formal insertion of CO_2 into the α-phosphino C–H bond of **14**, leading to a new five-membered ring in which the chelation via the oxygen atom of the ester function has been replaced by an oxygen atom of CO_2. The C(11)–C(12) bond formed in this reaction as a length of 1.43 (3) Å (average value) and may be assigned a partial double-bond character which makes even more striking the ease with which it can be reversibly formed and broken (eq 10). In **16** and **17**, electron delocalization occurs as in **13** or **14** but is now further extended to the exocyclic substituents. In the attempts made to isolate **16** in the solid state (vide supra), equilibrium 10 was displaced to the left because of the lower solubility of **13**. The opposite situation was met with **14** and **17**. The P–C(12) distance (1.80 (3) Å) is not significantly different from the other P–C distances, which are typical for usual phosphines. Because of the large σ values, other bond distances



13, ($\overline{\mathrm{C\;N}}$) = dmba

14, ($\overline{\mathrm{C\;N}}$) = 8-mq

16

17

will not be discussed in detail. The dihedral angle of the 8-mq ligand and the palladium square plane is 13°, the folding occuring along the NC(1) axis. All other atoms with the exception of the aromatic carbons of PPh_2 are almost coplanar (Table VIII). We can therefore suggest that the acidic proton observed in the NMR spectrum (at ca. 13.9 ppm) is located between O(2) and O(3), forming with them and C(11), C(12), and C(13) a planar six-membered ring with high electron delocalization.

The stacking of the two molecules in the asymmetric unit ("dimer") is such that the 8-mq moieties are parallel at a distance of 3.62 Å and are disposed in a way which bears some resemblance to the AB stacking of graphite (for which the AB distance is 3.35 Å). This is depicted in Figure 5. The H atom closest to the palladium is the ortho H(21) at 2.87 Å, illustrating the tendency[39] of palladium to interact with H atoms.

Reactions of CO_2 with organometallic complexes have aroused considerable interest over the last 5 years.[40] It has been recognized that CO_2 activation can indeed be achieved by means of transition-metal complexes. Insertions of CO_2 into transition-metal -H, -C, -N, and -O bonds have been reported. Some of them are reversible[29,40d,e,f,g,i,l] and very few involve C-C bond formation.[29,40d,f,h,j,k] Any structural information to be gained about the CO_2 activation at the metal center is of highest interest. Of the examples where a molecular structure of a CO_2 reaction product could be established by X-ray diffraction, only few were concerned with a reversible system,[40e,g,i] none of which involved C-C bond formation. We therefore conclude that the reaction with CO_2 described in this paper is the first example where the reversible CO_2 insertion in a molecular complex has been fully characterized by X-ray diffraction as resulting from a C-C coupling.

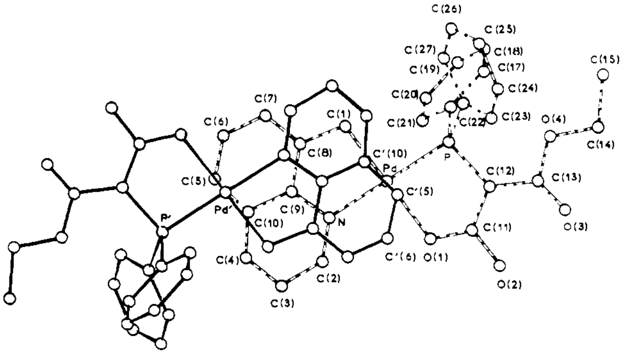
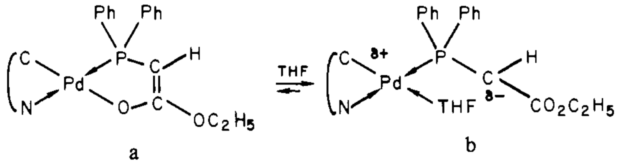


Figure 5. A top view showing the molecular stacking in the "dimer" 17. The bottom molecule is represented by dotted lines.

The following reasons might be invoked to explain the specific features of our system. CO_2 insertion results from the nucleophilic attack of CO_2 by the α-phosphino carbon which bears a labile H. Complexes **13** and **14** behave in THF as if the following situation were present.[41] The 1,3-dipolar form is favored by the



a

b

strong trans influence of the σ-bonded carbon atom of the cyclometalated ligand labilizing the Pd–O bond. This could explain why under the same conditions *cis*-Pt[$Ph_2PCHC(O)OC_2H_5]_2$ (**18**) (see Experimental Section) does not react with CO_2. The insertion products **16** and **17**, like their precursors, present a stable $\overline{\mathrm{P\;O}}$ five-membered ring on top of the ancillary ($\overline{\mathrm{C\;N}}$) chelate. The deinsertion of CO_2 in **16** and **17** is facilitated (i) again by the labilized Pd–O bond and (ii) by the presence of the electron-withdrawing ester group. The latter effect has been invoked by Saegusa and et al.[40f] in $NCCH_2CO_2Cu\cdot(PBu_3{}^n)_x$. Although our reversible CO_2 reaction involves very facile C–C and Pd–O bond formation or cleavage under ambient conditions, the free energy change for it is small.

The bifunctional activation of CO_2 presented in this paper proceeds from a nucleophilic carbon center reacting with the carbon atom of CO_2 and electrophilic centers (Pd and H^+) stabilizing the oxygen atoms of CO_2.

Acknowledgment. Thanks are due to the CNRS for a grant to D.M. and for financial help under GRECO P. We are grateful to Mrs. Kremp and Dr. R. Graff for their assistance in obtaining of the NMR spectra.

Supplementary Material Available: Positional and thermal parameters for **10**, **13**, and **17** (Tables XI, XII, and XIII), observed and calculated structure factors for **10**, **13**, and **17** (Tables XIV, XV, and XVI) (88 pages). Ordering information is given on any current masthead page.

---

[39] See, for example: Postel, M.; Pfeffer, M.; Riess, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 5623–5627.

[40] (a) Chatt, J.; Kubota, M.; Leigh, G. J.; March, F. C.; Yarrow, D. J. *J. Chem. Soc., Chem. Commun.* **1974**, 1033–1034. (b) Herskovitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615–1616. (c) Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* **1977**, 708–711. (d) English, A. D.; Herskovitz, T. *J. Am. Chem. Soc.* **1977**, *99*, 1648–1649. (e) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *Ibid.* **1978**, *100*, 7405–7407. (f) Tsuda, T.; Chujo, Y.; Saegusa, T. *Ibid.* **1978**, *100*, 630–632. (g) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *22*, L35–L36. (h) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577–7585. (i) Chisholm, M. H.; Cotton, F. A.; Extrine, M. W.; Reichert, W. W. *Ibid.* **1978**, *100*, 1727–1734. (j) Jolly, P. W.; Stobbe, S.; Wilke, G.; Goddard, R.; Krüger, C.; Sekutwoski, J. C.; Tsay, Y. H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 124–125. (k) Herskovitz, T. *J. Am. Chem. Soc.* **1977**, *99*, 2391–2392. (l) Tsuda, T.; Chujo, Y.; Saegusa, T. *Ibid.* **1980**, *102*, 431–433.

[41] The intermediate (dmba)Pd(Ph_2PCHCN) suggested in the formation of 8 might also have a b-type structure.